

The printed page, covered with atomic symbols, lines, and pairs of dots, makes it easy to forget the amazing, three-dimensional reality of molecular shape. In any molecule, each atom, bonding pair, and lone pair has its own position in space relative to the others, determined by the attractive and repulsive forces that govern all matter. With definite angles and distances between the nuclei, a molecule has a characteristic minute architecture, extending throughout its tiny volume of space. Whether we consider the details of simple reactions, the properties of synthetic materials, or the intricate life-sustaining processes of living cells, molecular shape is a crucial factor. In this chapter, we see how to depict molecules, first as two-dimensional drawings and then as three-dimensional objects.

## 10.1 DEPICTING MOLECULES AND IONS WITH LEWIS STRUCTURES

The first step toward visualizing what a molecule looks like is to convert its molecular formula to its **Lewis structure** (or **Lewis formula**).<sup>\*</sup> This two-dimensional structural formula consists of electron-dot symbols that depict each atom and its neighbors, the bonding pairs that hold them together, and the lone pairs that fill each atom's outer level (valence shell). In many cases, the octet rule (Section 9.1) guides us in allotting electrons to the atoms in a Lewis structure; in many other cases, however, we set the rule aside.

### Using the Octet Rule to Write Lewis Structures

To write a Lewis structure, we decide on the relative placement of the atoms in the molecule (or polyatomic ion)—that is, which atoms are adjacent and become bonded to each other—and distribute the total number of valence electrons as bonding and lone pairs. Let's begin by examining Lewis structures for species that “obey” the octet rule—those in which each atom fills its outer level with eight electrons (or two for hydrogen).

**Lewis Structures for Molecules with Single Bonds** First, we discuss the steps for writing Lewis structures for molecules that have only single bonds, using nitrogen trifluoride,  $\text{NF}_3$ , as an example. Figure 10.1 lays out the steps.

*Step 1. Place the atoms relative to each other.* For compounds of molecular formula  $\text{AB}_n$ , place the atom with *lower group number* in the center because it needs more electrons to attain an octet; usually, this is also the atom with the *lower electronegativity*. In  $\text{NF}_3$ , the N (Group 5A;  $\text{EN} = 3.0$ ) has five electrons and so needs three, whereas each F (Group 7A;  $\text{EN} = 4.0$ ) has seven and so needs only one; thus, N goes in the center with the three F atoms around it:



<sup>\*</sup>A Lewis *structure* may be more correctly called a Lewis *formula* because it provides information about the relative placement of atoms in a molecule or ion and shows which atoms are bonded to each other, but it does **not** indicate the three-dimensional shape. Nevertheless, use of the term Lewis *structure* is a convention that we follow.

### Concepts & Skills to Review Before You Study This Chapter

- electron configurations of main-group elements (Section 8.3)
- electron-dot symbols (Section 9.1)
- the octet rule (Section 9.1)
- bond order, bond length, and bond energy (Sections 9.3 and 9.4)
- polar covalent bonds and bond polarity (Section 9.5)

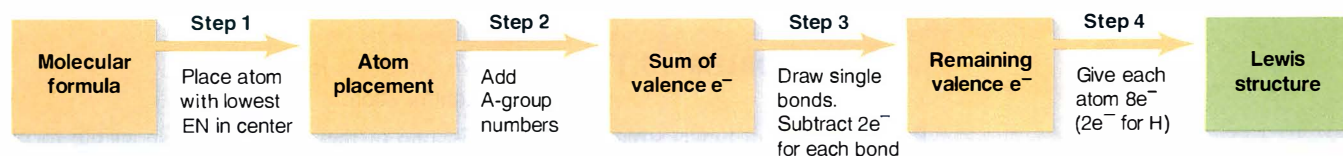


Figure 10.1 The steps in converting a molecular formula into a Lewis structure.

If the atoms have the same group number, as in  $\text{SO}_3$  or  $\text{ClF}_3$ , place the atom with the *higher period number* in the center. H can form only one bond, so it is *never* a central atom.

**Step 2. Determine the total number of valence electrons available.** For molecules, add up the valence electrons of all the atoms. (Recall that the number of valence electrons equals the A-group number.) In  $\text{NF}_3$ , N has five valence electrons, and each F has seven:

$$[1 \times \text{N}(5e^-)] + [3 \times \text{F}(7e^-)] = 5e^- + 21e^- = 26 \text{ valence } e^-$$

For polyatomic ions, *add* one  $e^-$  for each negative charge of the ion, or *subtract* one  $e^-$  for each positive charge.

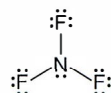
**Step 3. Draw a single bond from each surrounding atom to the central atom, and subtract two valence electrons for each bond.** There must be at least a single bond between bonded atoms:



Subtract  $2e^-$  for each single bond from the total number of valence electrons available (from step 2) to find the number remaining:

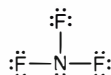
$$3 \text{ N}-\text{F bonds} \times 2e^- = 6e^- \quad \text{so} \quad 26e^- - 6e^- = 20e^- \text{ remaining}$$

**Step 4. Distribute the remaining electrons in pairs so that each atom ends up with eight electrons (or two for H).** First, place lone pairs on the *surrounding* (more electronegative) atoms to give each an octet. If any electrons remain, place them around the central atom. Then check that each atom has  $8e^-$ :



This is the Lewis structure for  $\text{NF}_3$ . Always check that the total number of electrons (bonds plus lone pairs) equals the sum of the valence electrons:  $6e^-$  in three bonds plus  $20e^-$  in ten lone pairs equals 26 valence electrons.

This particular arrangement of F atoms around an N atom resembles the molecular shape of  $\text{NF}_3$ , as you'll see when we discuss shapes in Section 10.2. But, Lewis structures do not indicate shape, so an equally correct depiction of  $\text{NF}_3$  is



or any other that retains the *same connections among the atoms*—a central N atom connected by single bonds to three surrounding F atoms.

Using these four steps, you can write a Lewis structure for any singly bonded molecule whose central atom is C, N, or O, as well as for some molecules with central atoms from higher periods. Remember that, in nearly all their compounds,

- Hydrogen atoms form one bond.
- Carbon atoms form four bonds.
- Nitrogen atoms form three bonds.
- Oxygen atoms form two bonds.
- Halogens form one bond when they are surrounding atoms; fluorine is always a surrounding atom.

### SAMPLE PROBLEM 10.1 Writing Lewis Structures for Molecules with One Central Atom

**Problem** Write a Lewis structure for  $\text{CCl}_2\text{F}_2$ , one of the compounds responsible for the depletion of stratospheric ozone.

**Solution** *Step 1.* Place the atoms relative to each other. In  $\text{CCl}_2\text{F}_2$ , carbon has the lowest group number and EN, so it is the central atom. The halogen atoms surround it, but their specific positions are not important (see margin).

*Step 2.* Determine the total number of valence electrons (from A-group numbers): C is in Group 4A, F is in Group 7A, and Cl is in Group 7A, too. Therefore, we have

$$[1 \times \text{C}(4e^-)] + [2 \times \text{F}(7e^-)] + [2 \times \text{Cl}(7e^-)] = 32 \text{ valence } e^-$$

*Step 3.* Draw single bonds to the central atom and subtract  $2e^-$  for each bond (see margin). Four single bonds use  $8e^-$ , so  $32e^- - 8e^-$  leaves  $24e^-$  remaining.

*Step 4.* Distribute the remaining electrons in pairs, beginning with the surrounding atoms, so that each atom has an octet (see margin).

**Check** Counting the electrons shows that each atom has an octet. Remember that bonding electrons are counted as belonging to each atom in the bond. The total number of electrons in bonds (8) and lone pairs (24) equals 32 valence electrons. Note that, as expected, C has four bonds and the surrounding halogens have one each.

**FOLLOW-UP PROBLEM 10.1** Write a Lewis structure for each of the following:

- (a)  $\text{H}_2\text{S}$       (b)  $\text{OF}_2$       (c)  $\text{SOCl}_2$

A slightly more complex situation occurs when molecules have two or more central atoms bonded to each other, with the other atoms around them.

### SAMPLE PROBLEM 10.2 Writing Lewis Structures for Molecules with More Than One Central Atom

**Problem** Write the Lewis structure for methanol, (molecular formula  $\text{CH}_4\text{O}$ ), an industrial alcohol that is also being considered as a gasoline alternative.

**Solution** *Step 1.* Place the atoms relative to each other. The H atoms can have only one bond, so C and O must be adjacent to each other. Recall that C has four bonds and O has two, so we arrange the H atoms to show this (see margin).

*Step 2.* Find the sum of valence electrons:

$$[1 \times \text{C}(4e^-)] + [1 \times \text{O}(6e^-)] + [4 \times \text{H}(1e^-)] = 14e^-$$

*Step 3.* Add single bonds and subtract  $2e^-$  for each bond (see margin). Five bonds use  $10e^-$ , so  $14e^- - 10e^-$  leaves  $4e^-$  remaining.

*Step 4.* Add the remaining electrons in pairs. Carbon already has an octet, and each H shares two electrons with the C; so the four remaining valence electrons form two lone pairs on O. We now have the Lewis structure for methanol (see margin).

**Check** Each H atom has  $2e^-$ , and the C and O each have  $8e^-$ . The total number of valence electrons is  $14e^-$ , which equals  $10e^-$  in bonds plus  $4e^-$  in lone pairs. Also note that each H has one bond, C has four, and O has two.

**FOLLOW-UP PROBLEM 10.2** Write a Lewis structure for each of the following:

- (a) hydroxylamine ( $\text{NH}_3\text{O}$ )      (b) dimethyl ether ( $\text{C}_2\text{H}_6\text{O}$ ; no  $\text{O}-\text{H}$  bonds)

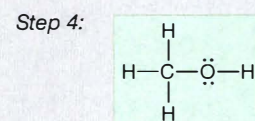
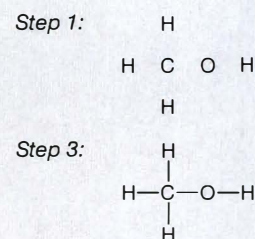
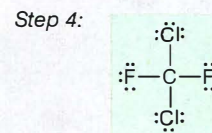
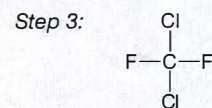
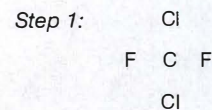
**Lewis Structures for Molecules with Multiple Bonds** Sometimes, you'll find that, after steps 1 to 4, there are not enough electrons for the central atom (or one of the central atoms) to attain an octet. This usually means that a multiple bond is present, and the following additional step is needed:

*Step 5. Cases involving multiple bonds.* If, after step 4, a central atom still does not have an octet, make a multiple bond by changing a lone pair from one of the surrounding atoms into a bonding pair to the central atom.

### SAMPLE PROBLEM 10.3 Writing Lewis Structures for Molecules with Multiple Bonds

**Problem** Write Lewis structures for the following:

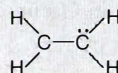
- (a) Ethylene ( $\text{C}_2\text{H}_4$ ), the most important reactant in the manufacture of polymers  
(b) Nitrogen ( $\text{N}_2$ ), the most abundant atmospheric gas



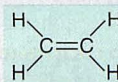


**Plan** We show the solution following steps 1 to 4: placing the atoms, counting the total valence electrons, making single bonds, and distributing the remaining valence electrons in pairs to attain octets. Then we continue with step 5, if needed.

**Solution** (a) For  $C_2H_4$ . After steps 1 to 4, we have



**Step 5.** Change a lone pair to a bonding pair. The C on the right has an octet, but the C on the left has only  $6e^-$ , so we convert the lone pair to another bonding pair between the two C atoms:



(b) For  $N_2$ . After steps 1 to 4, we have  $:\ddot{N}-\ddot{N}:$

**Step 5.** Neither N has an octet, so we change a lone pair to a bonding pair:  $:\ddot{N}=\ddot{N}:$

In this case, moving one lone pair to make a double bond still does not give the N on the right an octet, so we move a lone pair from the left N to make a triple bond:  $:\ddot{N}\equiv\ddot{N}:$

**Check** In part (a), each C has four bonds and counts the  $4e^-$  in the double bond as part of its own octet. The valence electron total is  $12e^-$ , all in six bonds. In part (b), each N has three bonds and counts the  $6e^-$  in the triple bond as part of its own octet. The valence electron total is  $10e^-$ , which equals the electrons in three bonds and two lone pairs.

**FOLLOW-UP PROBLEM 10.3** Write Lewis structures for each of the following:

(a) CO (the only common molecule in which C has only three bonds) (b) HCN (c)  $CO_2$

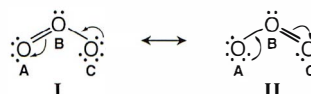
## Resonance: Delocalized Electron-Pair Bonding

We can often write more than one Lewis structure, each with the same relative placement of atoms, for a molecule or ion with *double bonds next to single bonds*. Consider ozone ( $O_3$ ), a serious air pollutant at ground level but a life-sustaining absorber of harmful ultraviolet (UV) radiation in the stratosphere. Two valid Lewis structures (with lettered O atoms for clarity) are



In structure I, oxygen B has a double bond to oxygen A and a single bond to oxygen C. In structure II, the single and double bonds are reversed. These are *not* two different  $O_3$  molecules, just different Lewis structures for the same molecule.

In fact, *neither* Lewis structure depicts  $O_3$  accurately. Bond length and bond energy measurements indicate that the two oxygen-oxygen bonds in  $O_3$  are identical, with properties that lie between those of an  $O-O$  bond and an  $O=O$  bond, something like a “one-and-a-half” bond. The molecule is shown more correctly with two Lewis structures, called **resonance structures** (or **resonance forms**), and a two-headed resonance arrow ( $\longleftrightarrow$ ) between them. Resonance structures *have the same relative placement of atoms but different locations of bonding and lone electron pairs*. You can convert one resonance form to another by moving lone pairs to bonding positions, and vice versa:

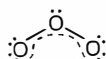


*Resonance structures are not real bonding depictions:*  $O_3$  does *not* change back and forth from structure I at one instant to structure II the next. The actual molecule is a **resonance hybrid**, an average of the resonance forms.

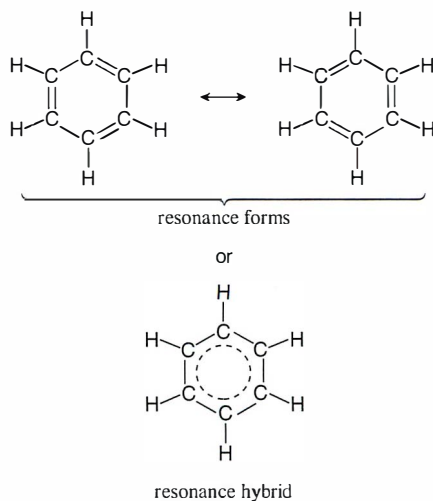
Consider these analogies. A mule is a genetic mix, a hybrid, of a horse and a donkey; it is not a horse one instant and a donkey the next. Similarly, the color

purple is a mix of two other colors, red and blue, not red one instant and blue the next (Figure 10.2). In the same sense, a resonance hybrid is one molecular species, not one resonance form this instant and another resonance form the next. The problem is that we cannot depict the hybrid accurately with a single Lewis structure.

Our need for more than one Lewis structure to depict the ozone molecule is the result of **electron-pair delocalization**. In a single, double, or triple bond, each electron pair is attracted by the nuclei of the two bonded atoms, and the electron density is greatest in the region between the nuclei: each electron pair is *localized*. In the resonance hybrid for  $\text{O}_3$ , however, two of the electron pairs (one bonding and one lone pair) are *delocalized*: their density is “spread” over the entire molecule. In  $\text{O}_3$ , this results in two identical bonds, each consisting of a single bond (the localized electron pair) and a *partial bond* (the contribution from one of the delocalized electron pairs). We draw the resonance hybrid with a curved dashed line to show the delocalized pairs:



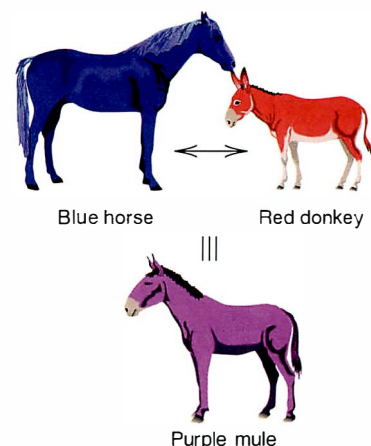
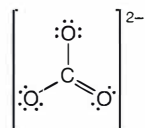
Electron delocalization diffuses electron density over a greater volume, which reduces electron-electron repulsions and thus stabilizes the molecule. Resonance is very common, and many molecules (and ions) are best depicted as resonance hybrids. Benzene ( $\text{C}_6\text{H}_6$ ), for example, has two important resonance forms in which alternating single and double bonds have different positions. The actual molecule has six identical carbon-carbon bonds because there are six  $\text{C}-\text{C}$  bonds and three electron pairs delocalized over all six  $\text{C}$  atoms, often shown as a dashed circle (or simply a circle):



Partial bonding, such as that occurring in resonance hybrids, often leads to fractional bond orders. For  $\text{O}_3$ , we have

$$\text{Bond order} = \frac{3 \text{ electron pairs}}{2 \text{ bonded-atom pairs}} = 1\frac{1}{2}$$

The carbon-to-carbon bond order in benzene is 9 electron pairs/6 bonded-atom pairs, or  $1\frac{1}{2}$  also. For the carbonate ion,  $\text{CO}_3^{2-}$ , three resonance structures can be drawn. Each has 4 electron pairs shared among 3 bonded-atom pairs, so the bond order is  $4/3$ , or  $1\frac{1}{3}$ . One of the three resonance structures for  $\text{CO}_3^{2-}$  is



**Figure 10.2** A purple mule, not a blue horse and a red donkey.





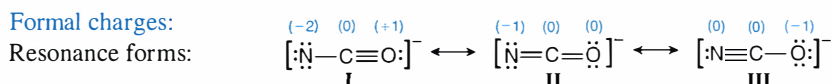
Forms I and II have the same formal charges but on different O atoms, so they contribute equally to the resonance hybrid. *Formal charges must sum to the actual charge on the species*: zero for a molecule and the ionic charge for an ion.

Note that, in form I, instead of the usual two bonds for oxygen, O<sub>B</sub> has three bonds and O<sub>C</sub> has one. Only when an atom has a zero formal charge does it have its usual number of bonds; the same holds for C in CO, N in NO<sub>3</sub><sup>−</sup>, and so forth.

Three criteria help us choose the more important resonance structures:

- Smaller formal charges (positive or negative) are preferable to larger ones.
- Like formal charges on adjacent atoms are not desirable.
- A more negative formal charge should reside on a more electronegative atom.

Let's apply these criteria next to the cyanate ion, NCO<sup>−</sup>, which has two different atoms around the central one. Three resonance forms with formal charges are



We eliminate form I because it has larger formal charges than the others and a positive formal charge on O, which is more electronegative than N. Forms II and III have the same magnitude of formal charges, but form III has a −1 charge on the more electronegative atom, O. Therefore, II and III are significant contributors to the resonance hybrid of the cyanate ion, but III is the more important.

Formal charge (used to examine resonance structures) is *not* the same as oxidation number (used to monitor redox reactions):

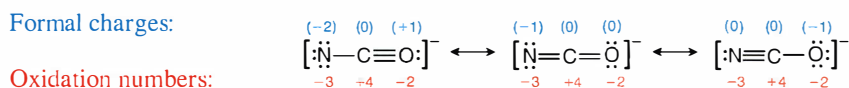
- For a formal charge, bonding electrons are assigned *equally* to the atoms (as if the bonding were *nonpolar covalent*), so each atom has half of them:

$$\text{Formal charge} = \text{valence } e^- - (\text{lone pair } e^- + \frac{1}{2} \text{ bonding } e^-)$$

- For an oxidation number, bonding electrons are assigned *completely* to the more electronegative atom (as if the bonding were *ionic*):

$$\text{Oxidation number} = \text{valence } e^- - (\text{lone pair } e^- + \text{bonding } e^-)$$

Here are the formal charges and oxidation numbers for the three cyanate ion resonance structures:



Note that the oxidation numbers *do not* change from one resonance form to another (because the electronegativities *do not* change), but the formal charges *do* change (because the numbers of bonding and lone pairs *do* change).

## Lewis Structures for Exceptions to the Octet Rule

The octet rule is a useful guide for most molecules with Period 2 central atoms, but not for every one. Also, many molecules have central atoms from higher periods. As you'll see, some central atoms have fewer than eight electrons around them, and others have more. The most significant octet rule exceptions are for molecules containing electron-deficient atoms, odd-electron atoms, and especially atoms with expanded valence shells.

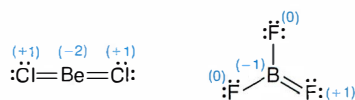
**Electron-Deficient Molecules** Gaseous molecules containing either beryllium or boron as the central atom are often **electron deficient**; that is, they have *fewer*



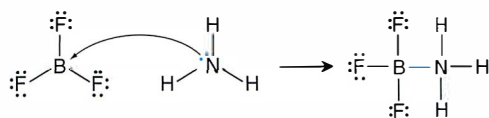
than eight electrons around the Be or B atom. The Lewis structures of gaseous beryllium chloride\* and boron trifluoride are



There are only four electrons around beryllium and six around boron. Why don't lone pairs from the surrounding halogen atoms form multiple bonds to the central atoms, thereby satisfying the octet rule? Halogens are much more electronegative than beryllium or boron, and formal charges show that the following are unlikely structures:

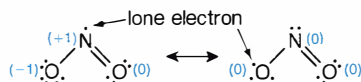


(Some data for  $\text{BF}_3$  show a shorter than expected B—F bond. Shorter bonds indicate double-bond character, so the structure with the B=F bond may be a minor contributor to a resonance hybrid.) The main way electron-deficient atoms attain an octet is by forming additional bonds in reactions. When  $\text{BF}_3$  reacts with ammonia, for instance, a compound forms in which boron attains its octet:

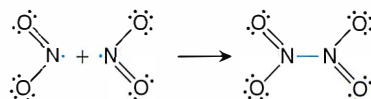


**Odd-Electron Molecules** A few molecules contain a central atom with an odd number of valence electrons, so they cannot possibly have all their electrons in pairs. Such species, called **free radicals**, contain a lone (unpaired) electron, which makes them paramagnetic (Section 8.5) and extremely reactive. Let's use formal charges to decide where the lone electron resides. Most odd-electron molecules have a central atom from an odd-numbered group, such as N [Group 5A(15)] or Cl [Group 7A(17)].

Consider nitrogen dioxide ( $\text{NO}_2$ ) as an example. A major contributor to urban smog is formed when the NO in auto exhaust is oxidized.  $\text{NO}_2$  has several resonance forms. Two involve the O atom that is doubly bonded, as in the case of ozone. Several others involve the location of the lone electron. Two of these resonance forms are shown below. The form with the lone electron on the singly bonded O has zero formal charges (right):



But the form with the lone electron on N (left) must be important also because of the way  $\text{NO}_2$  reacts. Free radicals react with each other to pair up their lone electrons. When two  $\text{NO}_2$  molecules collide, the lone electrons pair up to form the N—N bond in dinitrogen tetraoxide ( $\text{N}_2\text{O}_4$ ) and each N attains an octet:



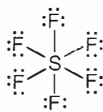
**Expanded Valence Shells** Many molecules and ions have more than eight valence electrons around the central atom. *An atom expands its valence shell to form more bonds*, a process that releases energy. A central atom can accommodate additional pairs by using empty *outer d* orbitals in addition to occupied *s* and *p* orbitals.

\*Even though beryllium is an alkaline earth metal [Group 2A(2)], most of its compounds have properties consistent with covalent, rather than ionic, bonding (Chapter 14). For example, molten  $\text{BeCl}_2$  does not conduct electricity, indicating the absence of ions.

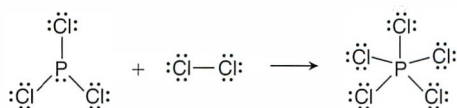


Therefore, **expanded valence shells** occur only with a *central nonmetal atom in which  $d$  orbitals are available, that is, one from Period 3 or higher*.

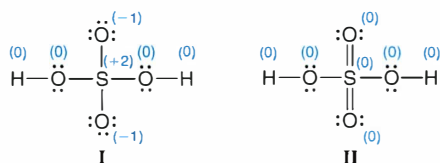
One example is sulfur hexafluoride,  $\text{SF}_6$ , a remarkably dense and inert gas used as an insulator in electrical equipment. The central sulfur is surrounded by six single bonds, one to each fluorine, for a total of 12 electrons:



Another example is phosphorus pentachloride,  $\text{PCl}_5$ , a fuming yellow-white solid used in the manufacture of lacquers and films.  $\text{PCl}_5$  is formed when phosphorus trichloride,  $\text{PCl}_3$ , reacts with chlorine gas. The P in  $\text{PCl}_3$  has an octet, but it uses the lone pair to form two more bonds to chlorine and expands its valence shell in  $\text{PCl}_5$  to a total of 10 electrons. Note that when  $\text{PCl}_5$  forms, *one* Cl—Cl bond breaks (left side of the equation), and *two* P—Cl bonds form (right side), for a net increase of one bond:



In  $\text{SF}_6$  and  $\text{PCl}_5$ , the central atom forms bonds to *more than four* atoms. But there are many cases of expanded valence shells in which the central atom bonds to *four or even fewer* atoms. Consider sulfuric acid, the industrial chemical produced in the greatest quantity. Two of the resonance forms for  $\text{H}_2\text{SO}_4$ , with formal charges, are



In form II, sulfur has an expanded valence shell of 12 electrons. Based on the formal charge rules, II contributes more than I to the resonance hybrid. More importantly, form II is consistent with observed bond lengths. In gaseous  $\text{H}_2\text{SO}_4$ , the two sulfur-oxygen bonds *with* H atoms attached to O are 157 pm long, whereas the two sulfur-oxygen bonds *without* H atoms attached to O are 142 pm long. This shorter bond length indicates double-bond character, which is shown in form II.

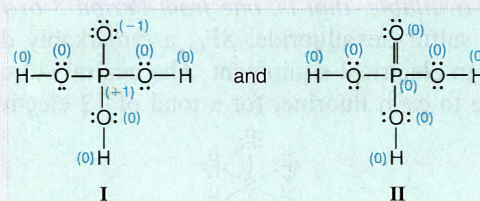
It's important to realize that formal charge is a useful, but not perfect, tool for assessing the importance of contributions to a resonance hybrid. You've already seen that it does not predict an important resonance form of  $\text{NO}_2$ . In fact, recent theoretical calculations indicate that, for many species with central atoms from Period 3 or higher, forms with expanded valence shells and zero formal charges may be less important than forms with higher formal charges. But we will continue to apply the formal charge rules because it is usually the simplest approach consistent with experimental data.

### SAMPLE PROBLEM 10.5 Writing Lewis Structures for Octet-Rule Exceptions

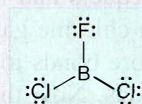
**Problem** Write Lewis structures for (a)  $\text{H}_3\text{PO}_4$  (pick the most likely structure); (b)  $\text{BFCl}_2$ .

**Plan** We write each Lewis structure and examine it for exceptions to the octet rule. In (a), the central atom is P, which is in Period 3, so it can use  $d$  orbitals to have more than an octet. Therefore, we can write more than one Lewis structure. We use formal charges to decide if one resonance form is more important. In (b), the central atom is B, which can have fewer than an octet of electrons.

**Solution** (a) For  $\text{H}_3\text{PO}_4$ , two possible Lewis structures, with formal charges, are



Structure II has lower formal charges, so it is the more important resonance form. (b) For  $\text{BFCl}_2$ , the Lewis structure leaves B with only six electrons surrounding it:



**Comment** In (a), structure II is also consistent with bond length measurements, which show one shorter (152 pm) phosphorus-oxygen bond and three longer (157 pm) ones.

**FOLLOW-UP PROBLEM 10.5** Write the most likely Lewis structure for (a)  $\text{POCl}_3$ ; (b)  $\text{ClO}_2$ ; (c)  $\text{XeF}_4$ .

## SECTION SUMMARY

A stepwise process is used to convert a molecular formula into a Lewis structure, a *two-dimensional* representation of a molecule (or ion) that shows the relative placement of atoms and distribution of valence electrons among bonding and lone pairs. When two or more Lewis structures can be drawn for the same relative placement of atoms, the actual structure is a hybrid of those resonance forms. Formal charges are often useful for determining the most important contributor to the hybrid. Electron-deficient molecules (central Be or B) and odd-electron species (free radicals) have less than an octet around the central atom but often attain an octet in reactions. In a molecule (or ion) with a central atom from Period 3 or higher, the atom can hold more than eight electrons by using *d* orbitals to expand its valence shell.

## 10.2 VALENCE-SHELL ELECTRON-PAIR REPULSION (VSEPR) THEORY AND MOLECULAR SHAPE

Virtually every biochemical process hinges to a great extent on the shapes of interacting molecules. Every medicine you take, odor you smell, or flavor you taste depends on part or all of one molecule fitting physically together with another. This universal importance of molecular shape in the functioning of each organism carries over to the ecosystem. Biologists have learned of complex interactions regulating behaviors (such as mating, defense, navigation, and feeding) that depend on one molecule's shape matching up with that of another. In this section, we discuss a model for understanding and predicting molecular shape.

The Lewis structure of a molecule is something like the blueprint of a building: a flat drawing showing the relative placement of parts (atom cores), structural connections (groups of bonding valence electrons), and various attachments (pairs of nonbonding valence electrons). To construct the molecular shape from the Lewis structure, chemists employ **valence-shell electron-pair repulsion (VSEPR) theory**. Its basic principle is that *each group of valence electrons around a central atom is located as far away as possible from the others in order to minimize repulsions*. We define a “group” of electrons as any number of electrons that occupy a localized region around an atom. Thus, an electron group may consist of a single bond, a double bond, a triple bond, a lone pair, or even a lone electron. [The two electron pairs in a double bond (or the three pairs in a triple

bond) occupy separate orbitals, so they remain near each other and act as one electron group, as you'll see in Chapter 11.] Each group of valence electrons around an atom repels the other groups to maximize the angles between them. It is the three-dimensional arrangement of nuclei joined by these groups that gives rise to the molecular shape.

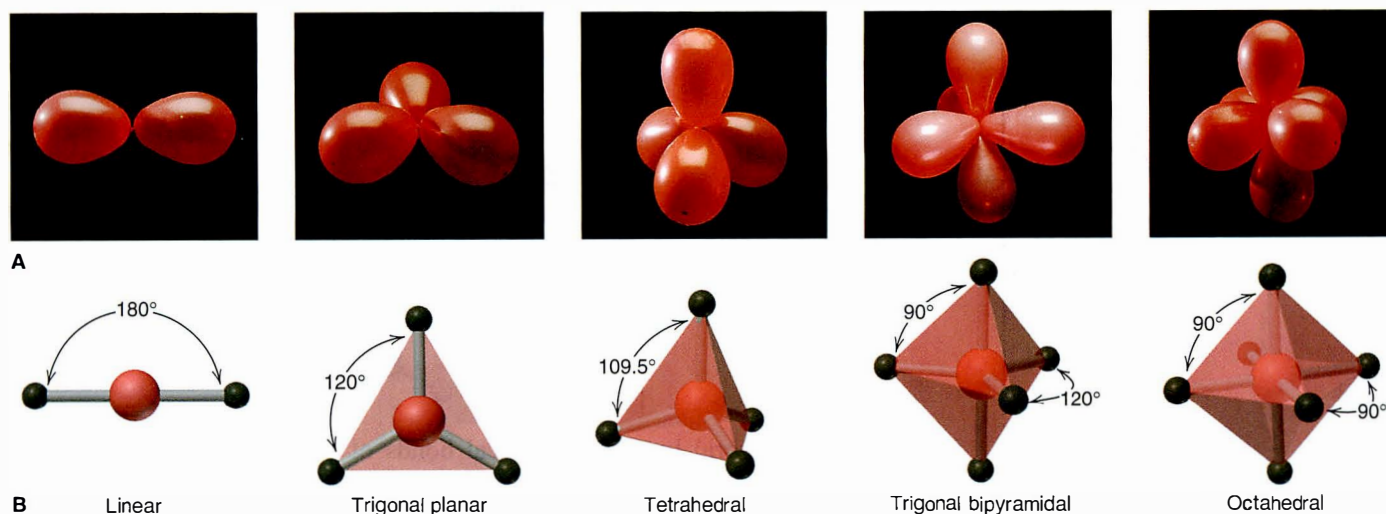
## Electron-Group Arrangements and Molecular Shapes

When two, three, four, five, or six objects attached to a central point maximize the space that each can occupy around that point, five geometric patterns result. Figure 10.3A depicts these patterns with balloons. If the objects are the valence-electron groups of a central atom, their repulsions maximize the space each occupies and give rise to the five *electron-group arrangements* of minimum energy seen in the great majority of molecules and polyatomic ions.

The electron-group arrangement is defined by the valence-electron groups, both bonding and nonbonding, around the central atom. On the other hand, the **molecular shape** is defined by the relative positions of the atomic nuclei. Figure 10.3B shows the molecular shapes that occur when *all* the surrounding electron groups are *bonding* groups. When some are *nonbonding* groups, different molecular shapes occur. Thus, *the same electron-group arrangement can give rise to different molecular shapes*: some with all bonding groups (as in Figure 10.3B) and others with bonding and nonbonding groups. To classify molecular shapes, we assign each a specific  $AX_mE_n$  designation, where  $m$  and  $n$  are integers, A is the central atom, X is a surrounding atom, and E is a nonbonding valence-electron group (usually a lone pair).

The **bond angle** is the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom at the vertex. The angles shown for the shapes in Figure 10.3B are *ideal* bond angles, those predicted by simple geometry alone. These are observed when all the bonding electron groups around a central atom are identical and are connected to atoms of the same element. When this is not the case, the bond angles deviate from the ideal angles, as you'll see shortly.

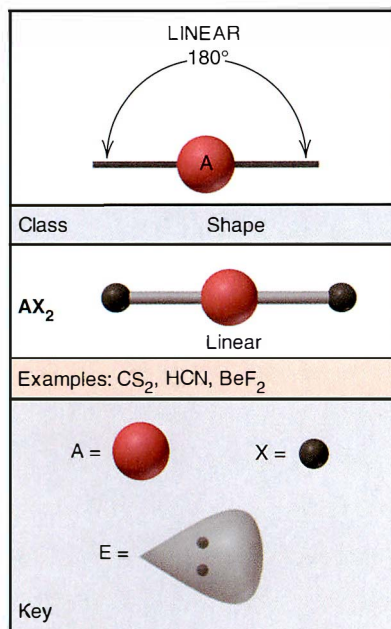
It's important to realize that we use the VSEPR model to account for the molecular shapes observed by means of various laboratory instruments. In almost



**Figure 10.3** Electron-group repulsions and the five basic molecular shapes. **A**, As an analogy for electron-group arrangements, two to six attached balloons form five geometric orientations such that each balloon occupies as much space as possible. **B**, Mutually repelling

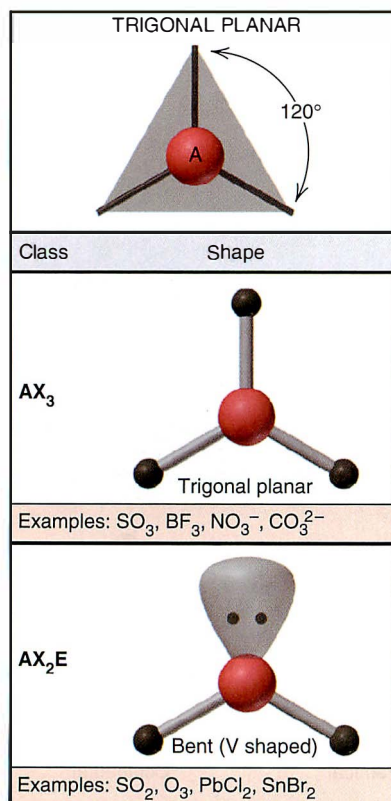
electron groups attached to a central atom (red) occupy as much space as possible. If each is a bonding group to a surrounding atom (dark gray), these molecular shapes and bond angles are observed. The shape has the same name as the electron-group arrangement.





**Figure 10.4** The single molecular shape of the linear electron-group arrangement. The key (bottom) for A, X, and E also refers to Figures 10.5, 10.6, 10.8, and 10.9.

Animation: VSEPR Theory and the Shape of Molecules  
Online Learning Center



**Figure 10.5** The two molecular shapes of the trigonal planar electron-group arrangement.

every case, VSEPR predictions are in accord with actual observations. (We discuss some of these observational methods in Chapter 12.)

## The Molecular Shape with Two Electron Groups (Linear Arrangement)

When two electron groups attached to a central atom are oriented as far apart as possible, they point in opposite directions. The **linear arrangement** of electron groups results in a molecule with a **linear shape** and a bond angle of 180°. Figure 10.4 shows the general form (top) and shape (middle) with VSEPR shape class ( $AX_2$ ), and the formulas of some linear molecules.

Gaseous beryllium chloride ( $BeCl_2$ ) is a linear molecule ( $AX_2$ ). Gaseous beryllium compounds are electron deficient, with only two electron pairs around the central Be atom:



In carbon dioxide, the central C atom forms two double bonds with the O atoms:

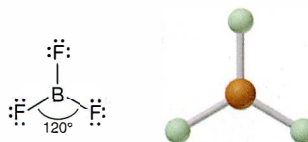


Each double bond acts as one electron group and is oriented 180° away from the other, so  $CO_2$  is linear. Notice that the lone pairs on the O atoms of  $CO_2$  or on the Cl atoms of  $BeCl_2$  are not involved in the molecular shape: only electron groups around the *central* atom influence shape.

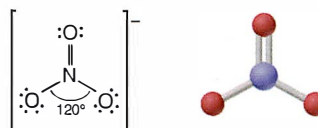
## Molecular Shapes with Three Electron Groups (Trigonal Planar Arrangement)

Three electron groups around the central atom repel each other to the corners of an equilateral triangle, which gives the **trigonal planar arrangement**, shown in Figure 10.5, and an ideal bond angle of 120°. This arrangement has two possible molecular shapes, one with three surrounding atoms and the other with two atoms and one lone pair. It provides our first opportunity to see the effects of double bonds and lone pairs on bond angles.

When the three electron groups are bonding groups, the molecular shape is *trigonal planar* ( $AX_3$ ). Boron trifluoride ( $BF_3$ ), another electron-deficient molecule, is an example. It has six electrons around the central B atom in three single bonds to F atoms. The nuclei lie in a plane, and each  $F-B-F$  angle is 120°:



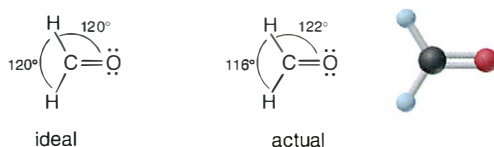
The nitrate ion ( $NO_3^-$ ) is one of several polyatomic ions with the trigonal planar shape. One of three resonance forms of the nitrate ion (Sample Problem 10.4) is



The resonance hybrid has three identical bonds of bond order  $1\frac{1}{3}$ , so the ideal bond angle is observed.

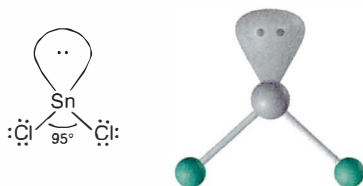
**Effect of Double Bonds** How do bond angles deviate from the ideal angles when the surrounding atoms and electron groups are not identical? Consider formaldehyde ( $CH_2O$ ), a substance with many uses, including the manufacture of Formica countertops, the production of methanol, and the preservation of cadavers. Its

trigonal planar shape is due to two types of surrounding atoms (O and H) and two types of electron groups (single and double bonds):



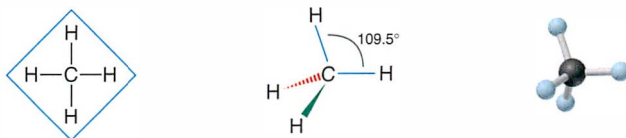
The actual bond angles deviate from the ideal because *the double bond, with its greater electron density, repels the two single bonds more strongly than they repel each other*. Note that the H—C—H bond angle is less than 120°.

**Effect of Lone Pairs** The molecular shape is defined *only* by the positions of the nuclei, so when one of the three electron groups is a lone pair (AX<sub>2</sub>E), the shape is **bent**, or **V shaped**, not trigonal planar. Gaseous tin(II) chloride is an example, with the three electron groups in a trigonal plane and the lone pair at one of the triangle's corners. A lone pair can have a major effect on bond angle. Because a lone pair is held by only one nucleus, it is less confined and exerts stronger repulsions than a bonding pair. Thus, *a lone pair repels bonding pairs more strongly than bonding pairs repel each other*. This stronger repulsion *decreases* the angle between bonding pairs. Note the decrease from the ideal 120° angle in SnCl<sub>2</sub>:



## Molecular Shapes with Four Electron Groups (Tetrahedral Arrangement)

The shapes described so far have all been easy to depict in two dimensions, but four electron groups must use three dimensions to achieve maximal separation. Recall that *Lewis structures do not depict shape*. Consider methane. The Lewis structure shown below (left) indicates four bonds pointing to the corners of a square, which suggests a 90° bond angle. However, in three dimensions, the four electron groups move farther apart and point to the vertices of a tetrahedron, a polyhedron with four faces made of identical equilateral triangles. Methane has a bond angle of 109.5°. Perspective drawings, such as the one shown below (middle) for methane, indicate depth by using solid and dashed wedges for some of the bonds: The ball-and-stick model (right) shows the tetrahedral shape clearly.

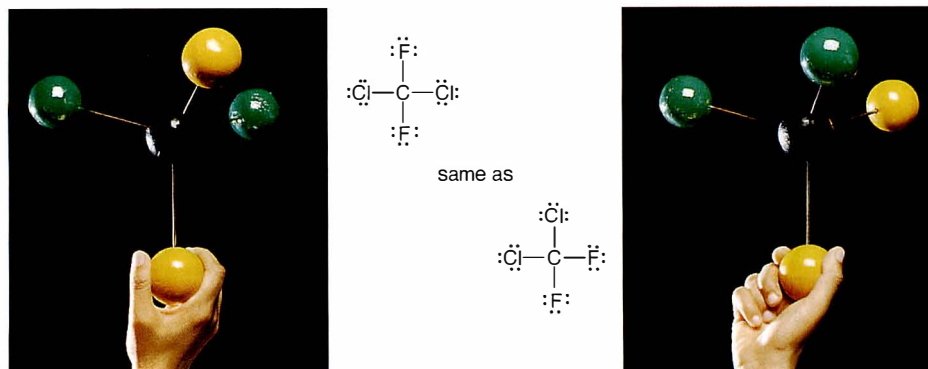


In a *perspective drawing* (middle), the normal bond lines (blue) represent bonds in the plane of the page; the solid wedge (green) is the bond between the atom in the plane of the page and a group lying toward you above the page; and the dashed wedge (red) is the bond to a group lying away from you below the page. The ball-and-stick model (right) shows the tetrahedral shape clearly.

*All molecules or ions with four electron groups around a central atom adopt the tetrahedral arrangement* (Figure 10.6). When all four electron groups are bonding groups, as in the case of methane, the molecular shape is also *tetrahedral* (AX<sub>4</sub>), a very common geometry in organic molecules. In Sample Problem 10.1, we drew the Lewis structure for the tetrahedral molecule dichlorodifluoromethane

Class	Shape
AX <sub>4</sub>	 Tetrahedral
Examples: CH <sub>4</sub> , SiCl <sub>4</sub> , SO <sub>4</sub> <sup>2-</sup> , ClO <sub>4</sub> <sup>-</sup>	
AX <sub>3</sub> E	 Trigonal pyramidal
Examples: NH <sub>3</sub> , PF <sub>3</sub> , ClO <sub>3</sub> <sup>-</sup> , H <sub>3</sub> O <sup>+</sup>	
AX <sub>2</sub> E <sub>2</sub>	 Bent (V shaped)
Examples: H <sub>2</sub> O, OF <sub>2</sub> , SCl <sub>2</sub>	

**Figure 10.6** The three molecular shapes of the tetrahedral electron-group arrangement.

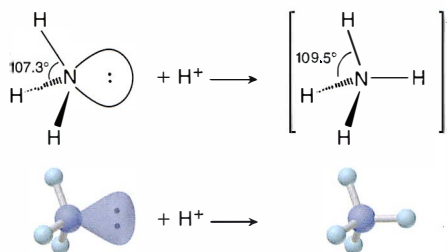


**Figure 10.7** Lewis structures and molecular shapes. Lewis structures do not indicate geometry. For example, it may seem as if two different Lewis structures can be written for  $\text{CCl}_2\text{F}_2$ , but a twist of the model (Cl, green; F, yellow) shows that they represent the same molecule.

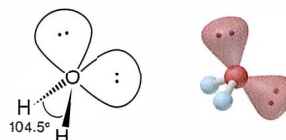
( $\text{CCl}_2\text{F}_2$ ), without regard to how the halogen atoms surround the carbon atom. Because Lewis structures are flat, it may seem as if we can write two different structures for  $\text{CCl}_2\text{F}_2$ , but these actually represent the same molecule, as Figure 10.7 makes clear.

When one of the four electron groups in the tetrahedral arrangement is a lone pair, the molecular shape is that of a **trigonal pyramid** ( $\text{AX}_3\text{E}$ ), a tetrahedron with one vertex “missing.” As we would expect from the stronger repulsions due to the lone pair, the measured bond angle is slightly less than the ideal  $109.5^\circ$ . In ammonia ( $\text{NH}_3$ ), for example, the lone pair forces the  $\text{N}-\text{H}$  bonding pairs closer, and the  $\text{H}-\text{N}-\text{H}$  bond angle is  $107.3^\circ$ .

Picturing molecular shapes is a great way to visualize what happens during a reaction. For instance, when ammonia accepts the proton from an acid, the lone pair on the N atom of trigonal pyramidal  $\text{NH}_3$  forms a covalent bond to the  $\text{H}^+$  and yields the ammonium ion ( $\text{NH}_4^+$ ), one of many tetrahedral polyatomic ions. Note how the  $\text{H}-\text{N}-\text{H}$  bond angle expands from  $107.3^\circ$  in  $\text{NH}_3$  to  $109.5^\circ$  in  $\text{NH}_4^+$ , as the lone pair becomes another bonding pair:



When the four electron groups around the central atom include two bonding and two nonbonding groups, the molecular shape is *bent*, or *V shaped* ( $\text{AX}_2\text{E}_2$ ). [In the trigonal planar arrangement, the shape with two bonding groups and one lone pair ( $\text{AX}_2\text{E}$ ) is also called bent, but its ideal bond angle is  $120^\circ$ , not  $109.5^\circ$ .] Water is the most important V-shaped molecule with the tetrahedral arrangement. We might expect the repulsions from its two lone pairs to have a *greater* effect on the bond angle than the repulsions from the single lone pair in  $\text{NH}_3$ . Indeed, the  $\text{H}-\text{O}-\text{H}$  bond angle is  $104.5^\circ$ , even less than the  $\text{H}-\text{N}-\text{H}$  angle in  $\text{NH}_3$ :





Thus, for similar molecules within a given electron-group arrangement, electron-pair repulsions cause deviations from ideal bond angles in the following order:

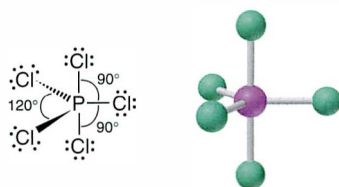
Lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair (10.2)

## Molecular Shapes with Five Electron Groups (Trigonal Bipyramidal Arrangement)

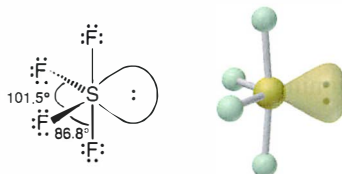
All molecules with five or six electron groups have a central atom from Period 3 or higher because only these atoms have the *d* orbitals available to expand the valence shell beyond eight electrons.

When five electron groups maximize their separation, they form the **trigonal bipyramidal arrangement**. In a trigonal bipyramid, two trigonal pyramids share a common base, as shown in Figure 10.8. Note that, in a molecule with this arrangement, *there are two types of positions for surrounding electron groups and two ideal bond angles*. Three **equatorial groups** lie in a trigonal plane that includes the central atom, and two **axial groups** lie above and below this plane. Therefore, a  $120^\circ$  bond angle separates equatorial groups, and a  $90^\circ$  angle separates axial from equatorial groups. In general, the greater the bond angle, the weaker the repulsions, so *equatorial-equatorial ( $120^\circ$ ) repulsions are weaker than axial-equatorial ( $90^\circ$ ) repulsions*. The tendency of the electron groups to occupy *equatorial positions*, and thus minimize the stronger axial-equatorial repulsions, governs the four shapes of the trigonal bipyramidal arrangement.

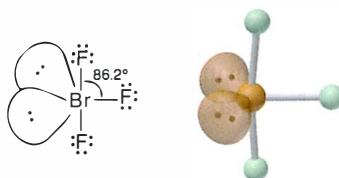
With all five positions occupied by bonded atoms, the molecule has the *trigonal bipyramidal shape* ( $AX_5$ ), as in phosphorus pentachloride ( $PCl_5$ ):



Three other shapes arise for molecules with lone pairs. Lone pairs exert stronger repulsions than bonding pairs, so *lone pairs occupy equatorial positions*. With one lone pair present at an equatorial position, the molecule has a **seesaw shape** ( $AX_4E$ ). Sulfur tetrafluoride ( $SF_4$ ), a powerful fluorinating agent, has this shape, shown here and in Figure 10.8 with the “seesaw” tipped up on an end. Note how the equatorial lone pair repels all four bonding pairs to reduce the bond angles:



The tendency of lone pairs to occupy equatorial positions causes molecules with three bonding groups and two lone pairs to have a **T shape** ( $AX_3E_2$ ). Bromine trifluoride ( $BrF_3$ ), one of many compounds with fluorine bonded to a larger halogen, has this shape. Note the predicted decrease from the ideal  $90^\circ$  F—Br—F bond angle:

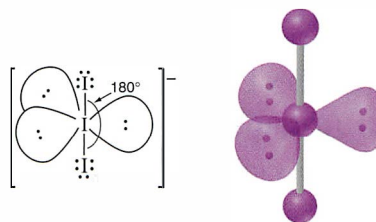


Molecules with three lone pairs in equatorial positions must have the two bonding groups in axial positions, which gives the molecule a **linear shape** ( $AX_2E_3$ ) and

TRIGONAL BIPYRAMIDAL	
Class	Shape
$AX_5$	 Trigonal bipyramidal
Examples: $PF_5$ , $AsF_5$ , $SOF_4$	
$AX_4E$	 Seesaw
Examples: $SF_4$ , $XeO_2F_2$ , $IF_4^+$ , $IO_2F_2^-$	
$AX_3E_2$	 T shaped
Examples: $ClF_3$ , $BrF_3$	
$AX_2E_3$	 Linear
Examples: $XeF_2$ , $I_3^-$ , $IF_2^-$	

**Figure 10.8** The four molecular shapes of the trigonal bipyramidal electron-group arrangement.

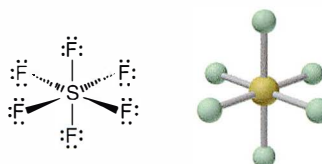
a  $180^\circ$  axial-to-central-to-axial (X—A—X) bond angle. For example, the triiodide ion ( $\text{I}_3^-$ ), which forms when  $\text{I}_2$  dissolves in aqueous  $\text{I}^-$  solution, is linear:



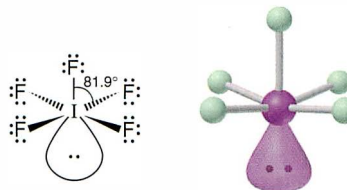
## Molecular Shapes with Six Electron Groups (Octahedral Arrangement)

The last of the five major electron-group arrangements is the **octahedral arrangement**. An octahedron is a polyhedron with eight faces made of identical equilateral triangles and six identical vertices, as shown in Figure 10.9. In a molecule (or ion) with this arrangement, six electron groups surround the central atom and each points to one of the six vertices, which gives all the groups a  $90^\circ$  ideal bond angle. Three important molecular shapes occur with this arrangement.

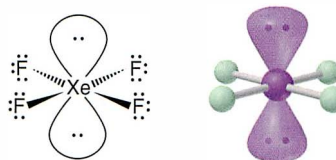
With six bonding groups, the molecular shape is *octahedral* ( $\text{AX}_6$ ), as in sulfur hexafluoride ( $\text{SF}_6$ ):



Because all six electron groups have the same ideal bond angle, it makes no difference which position one lone pair occupies. Five bonded atoms and one lone pair define the **square pyramidal shape** ( $\text{AX}_5\text{E}$ ), as in iodine pentafluoride ( $\text{IF}_5$ ):



When a molecule has four bonded atoms and two lone pairs, however, the lone pairs always lie at *opposite vertices* to avoid the stronger  $90^\circ$  lone pair–lone pair repulsions. This positioning gives the **square planar shape** ( $\text{AX}_4\text{E}_2$ ), as in xenon tetrafluoride ( $\text{XeF}_4$ ):



## Using VSEPR Theory to Determine Molecular Shape

Let's apply a stepwise method for using the VSEPR theory to determine a molecular shape from a molecular formula:

**Step 1.** Write the Lewis structure from the molecular formula (Figure 10.1) to see the relative placement of atoms and the number of electron groups.

**Step 2.** Assign an electron-group arrangement by counting *all* electron groups around the central atom, bonding *plus* nonbonding.

Class	Shape
$\text{AX}_6$	<p>Octahedral</p>
Examples: $\text{SF}_6$ , $\text{IOF}_5$	
$\text{AX}_5\text{E}$	<p>Square pyramidal</p>
Examples: $\text{BrF}_5$ , $\text{TeF}_5^-$ , $\text{XeOF}_4$	
$\text{AX}_4\text{E}_2$	<p>Square planar</p>
Examples: $\text{XeF}_4$ , $\text{ICl}_4^-$	

**Figure 10.9** The three molecular shapes of the octahedral electron-group arrangement.

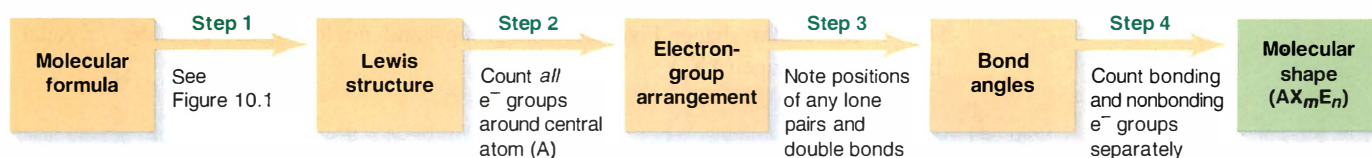


*Step 3. Predict the ideal bond angle from the electron-group arrangement and the direction of any deviation caused by lone pairs or double bonds.*

*Step 4. Draw and name the molecular shape by counting bonding groups and nonbonding groups separately.*

Figure 10.10 summarizes these steps, and the next two sample problems apply them.

**Figure 10.10** The steps in determining a molecular shape. Four steps are needed to convert a molecular formula to a molecular shape.



### SAMPLE PROBLEM 10.6 Predicting Molecular Shapes with Two, Three, or Four Electron Groups

**Problem** Draw the molecular shapes and predict the bond angles (relative to the ideal angles) of (a)  $\text{PF}_3$  and (b)  $\text{COCl}_2$ .

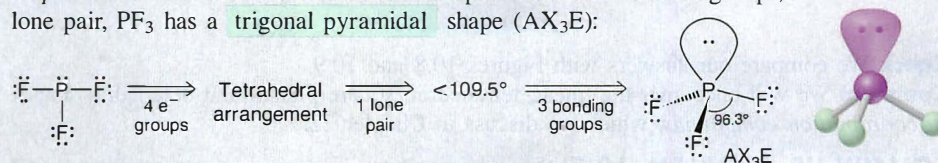
**Solution** (a) For  $\text{PF}_3$ .

*Step 1.* Write the Lewis structure from the formula (see below left).

*Step 2.* Assign the electron-group arrangement: Three bonding groups plus one lone pair give four electron groups around P and the *tetrahedral arrangement*.

*Step 3.* Predict the bond angle: For the tetrahedral electron-group arrangement, the ideal bond angle is  $109.5^\circ$ . There is one lone pair, so the actual bond angle should be less than  $109.5^\circ$ .

*Step 4.* Draw and name the molecular shape: With four electron groups, one of them a lone pair,  $\text{PF}_3$  has a *trigonal pyramidal* shape ( $\text{AX}_3\text{E}$ ):



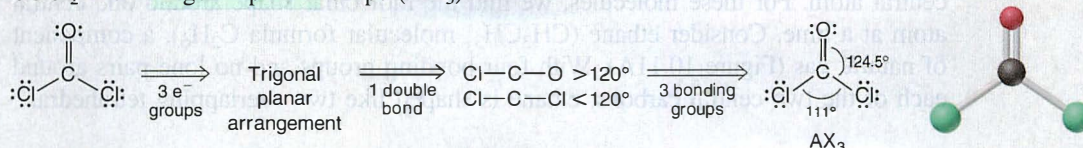
(b) For  $\text{COCl}_2$ .

*Step 1.* Write the Lewis structure from the formula (see below left).

*Step 2.* Assign the electron-group arrangement: Two single bonds plus one double bond give three electron groups around C and the *trigonal planar arrangement*.

*Step 3.* Predict the bond angles: The ideal bond angle is  $120^\circ$ , but the double bond between C and O should compress the  $\text{Cl}-\text{C}-\text{Cl}$  angle to less than  $120^\circ$ .

*Step 4.* Draw and name the molecular shape: With three electron groups and no lone pairs,  $\text{COCl}_2$  has a *trigonal planar* shape ( $\text{AX}_3$ ):



**Check** We compare the answers with the information in Figures 10.5 and 10.6.

**Comment** Be sure the Lewis structure is correct because it determines the other steps.

**FOLLOW-UP PROBLEM 10.6** Draw the molecular shapes and predict the bond angles (relative to the ideal angles) of (a)  $\text{CS}_2$ ; (b)  $\text{PbCl}_2$ ; (c)  $\text{CBr}_4$ ; (d)  $\text{SF}_2$ .

### SAMPLE PROBLEM 10.7 Predicting Molecular Shapes with Five or Six Electron Groups

**Problem** Determine the molecular shapes and predict the bond angles (relative to the ideal angles) of (a)  $\text{SbF}_5$  and (b)  $\text{BrF}_5$ .

**Plan** We proceed as in Sample Problem 10.6, keeping in mind the need to minimize the number of  $90^\circ$  repulsions.



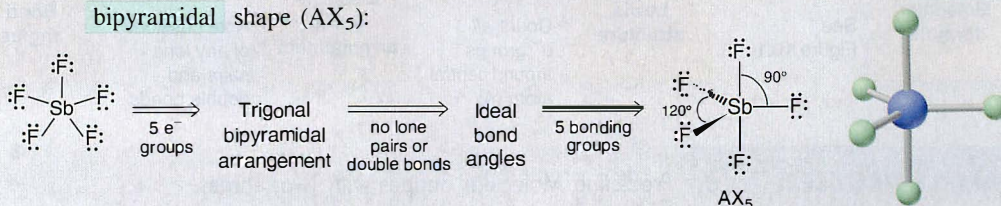
**Solution (a)** For  $\text{SbF}_5$ .

*Step 1.* Lewis structure (see below left).

*Step 2.* Electron-group arrangement: With five electron groups, this is the *trigonal bipyramidal* arrangement.

*Step 3.* Bond angles: All the groups and surrounding atoms are identical, so the bond angles are ideal:  $120^\circ$  between equatorial groups and  $90^\circ$  between axial and equatorial groups.

*Step 4.* Molecular shape: Five electron groups and no lone pairs give the *trigonal bipyramidal* shape ( $\text{AX}_5$ ):

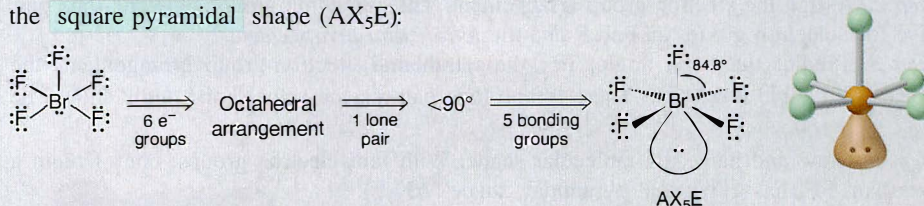
**(b)** For  $\text{BrF}_5$ .

*Step 1.* Lewis structure (see below left).

*Step 2.* Electron-group arrangement: Six electron groups give the *octahedral* arrangement.

*Step 3.* Bond angles: The lone pair should make all bond angles less than the ideal  $90^\circ$ .

*Step 4.* Molecular shape: With six electron groups and one of them a lone pair,  $\text{BrF}_5$  has the *square pyramidal* shape ( $\text{AX}_5\text{E}$ ):



**Check** We compare our answers with Figures 10.8 and 10.9.

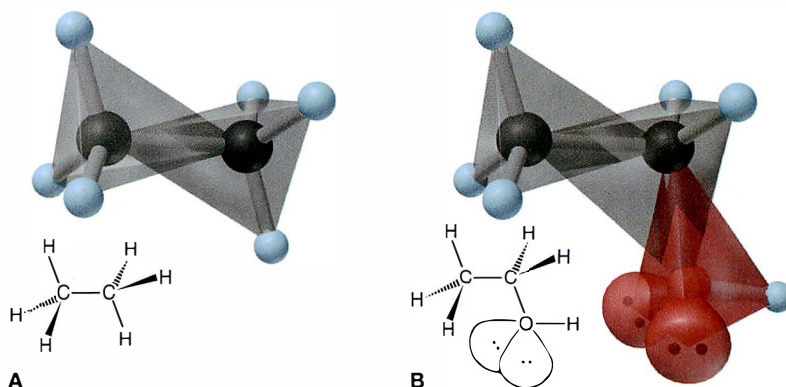
**Comment** We will encounter the linear, tetrahedral, square planar, and octahedral shapes in *coordination compounds*, which we discuss in Chapter 22.

**FOLLOW-UP PROBLEM 10.7** Draw the molecular shapes and predict the bond angles (relative to the ideal angles) of (a)  $\text{ICl}_2^-$ ; (b)  $\text{ClF}_3$ ; (c)  $\text{SOF}_4$ .

## Molecular Shapes with More Than One Central Atom

Many molecules, especially those in living systems, have more than one central atom. The shapes of these molecules are combinations of the molecular shapes for each central atom. For these molecules, we find the molecular shape around one central atom at a time. Consider ethane ( $\text{CH}_3\text{CH}_3$ ; molecular formula  $\text{C}_2\text{H}_6$ ), a component of natural gas (Figure 10.11A). With four bonding groups and no lone pairs around each of the two central carbons, ethane is shaped like two overlapping tetrahedra.

**Figure 10.11** The tetrahedral centers of ethane and of ethanol. When a molecule has more than one central atom, the overall shape is a composite of the shape around each center. **A**, Ethane's shape can be viewed as two overlapping tetrahedra. **B**, Ethanol's shape can be viewed as three overlapping tetrahedral arrangements, with the shape around the O atom bent (V shaped) because of its two lone pairs.



Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ; molecular formula  $\text{C}_2\text{H}_6\text{O}$ ), the intoxicating substance in beer and wine, has three central atoms (Figure 10.11B). The  $\text{CH}_3$ — group is tetrahedrally shaped, and the — $\text{CH}_2$ — group has four bonding groups around its central C atom, so it is tetrahedrally shaped also. The O atom has four electron groups and two lone pairs around it, which gives the V shape ( $\text{AX}_2\text{E}_2$ ).

### SAMPLE PROBLEM 10.8 Predicting Molecular Shapes with More Than One Central Atom

**Problem** Determine the shape around each of the central atoms in acetone,  $(\text{CH}_3)_2\text{C}=\text{O}$ .

**Plan** There are three central atoms, all C, two of which are in  $\text{CH}_3$ — groups. We determine the shape around one central atom at a time.

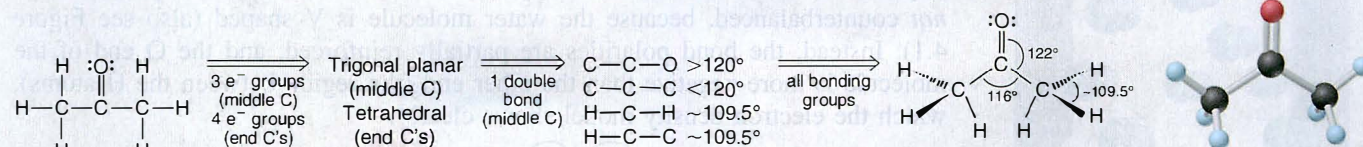
#### Solution

**Step 1.** Lewis structure (see below left).

**Step 2.** Electron-group arrangement: Each  $\text{CH}_3$ — group has four electron groups around its central C, so its electron-group arrangement is *tetrahedral*. The third C atom has three electron groups around it, so it has the *trigonal planar* arrangement.

**Step 3.** Bond angles: The  $\text{H—C—H}$  angle in the  $\text{CH}_3$ — groups should be near the ideal tetrahedral angle of  $109.5^\circ$ . The  $\text{C}=\text{O}$  double bond should compress the  $\text{C—C—C}$  angle to less than the ideal  $120^\circ$ .

**Step 4.** Shapes around central atoms: With four electron groups and no lone pairs, the shapes around the two C atoms in the  $\text{CH}_3$ — groups are *tetrahedral* ( $\text{AX}_4$ ). With three electron groups and no lone pairs, the shape around the middle C atom is *trigonal planar* ( $\text{AX}_3$ ):



**FOLLOW-UP PROBLEM 10.8** Determine the shape around each central atom and predict any deviations from ideal bond angles in the following: (a)  $\text{H}_2\text{SO}_4$ ; (b) propyne ( $\text{C}_3\text{H}_4$ ; there is one  $\text{C}\equiv\text{C}$  bond); (c)  $\text{S}_2\text{F}_2$ .

## SECTION SUMMARY

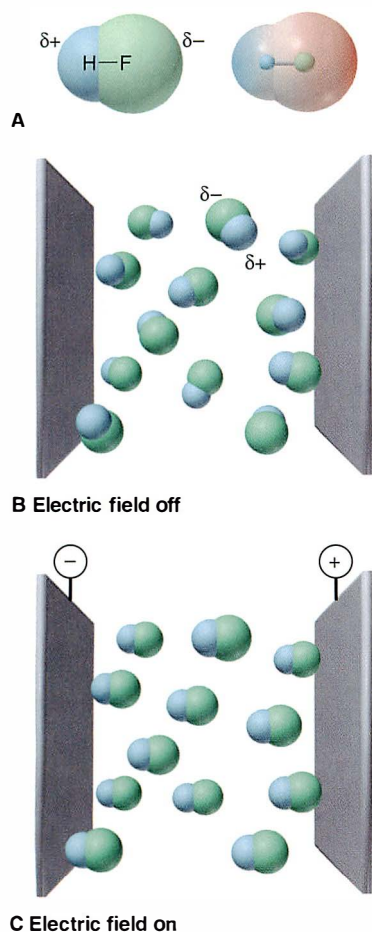
The VSEPR theory proposes that each group of electrons (single bond, multiple bond, lone pair, or lone electron) around a central atom remains as far away from the others as possible. One of five electron-group arrangements results when two, three, four, five, or six electron groups surround a central atom. Each arrangement is associated with one or more molecular shapes. Ideal bond angles are prescribed by the regular geometric shapes; deviations from these angles occur when the surrounding atoms or electron groups are not identical. Lone pairs and double bonds exert greater repulsions than single bonds. Larger molecules have shapes that are composites of the shapes around each central atom.

## 10.3 MOLECULAR SHAPE AND MOLECULAR POLARITY

Knowing the shape of a substance's molecules is a key to understanding its physical and chemical behavior. One of the most important and far-reaching effects of molecular shape is molecular polarity, which can influence melting and boiling points, solubility, chemical reactivity, and even biological function.

In Chapter 9, you learned that a covalent bond is *polar* when it joins atoms of different electronegativities because the atoms share the electrons unequally. In diatomic molecules, such as  $\text{HF}$ , where there is only one bond, the bond polarity causes the molecule itself to be polar. Molecules with a net imbalance of charge have a **molecular polarity**. In molecules with more than two atoms, *both shape and bond polarity determine molecular polarity*. In an electric field, polar molecules become





**Figure 10.12** The orientation of polar molecules in an electric field. **A**, A space-filling model of HF (*left*) shows the partial charges of this polar molecule. The electron density model (*right*) shows high electron density (*red*) associated with the F end and low electron density (*blue*) with the H end. **B**, In the absence of an external electric field, HF molecules are oriented randomly. **C**, In the presence of an electric field, the molecules, on average, become oriented with their partial charges pointing toward the oppositely charged plates.

oriented, on average, with their partial charges pointing toward the oppositely charged electric plates, as shown for HF in Figure 10.12. The **dipole moment** ( $\mu$ ) is the product of these partial charges and the distance between them. It is typically measured in *debye* (D) units; using the SI units of charge (coulomb, C) and length (meter, m),  $1 \text{ D} = 3.34 \times 10^{-30} \text{ C}\cdot\text{m}$ . [The unit is named for Peter Debye (1884–1966), the Dutch American chemist and physicist who won a Nobel Prize in 1936 for his major contributions to our understanding of molecular structure and solution behavior.]

To determine molecular polarity, we also consider shape because the presence of polar bonds does not *always* lead to a polar molecule. In carbon dioxide, for example, the large electronegativity difference between C (EN = 2.5) and O (EN = 3.5) makes each C=O bond quite polar. However,  $\text{CO}_2$  is linear, so its bonds point  $180^\circ$  from each other. As a result, the two identical bond polarities are counterbalanced and give the molecule *no net dipole moment* ( $\mu = 0 \text{ D}$ ). The electron density model shows regions of high negative charge (*red*) distributed equally on either side of the central region of high positive charge (*blue*):

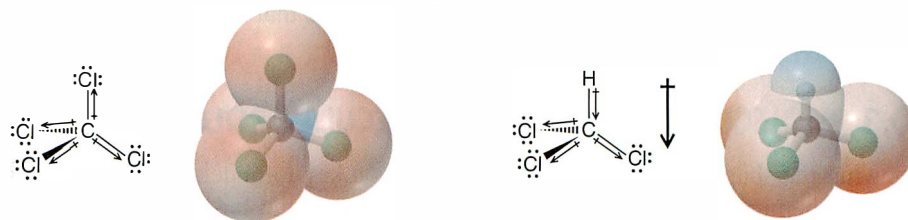


Water also has identical atoms bonded to the central atom, but it *does* have a significant dipole moment ( $\mu = 1.85 \text{ D}$ ). In each O—H bond, electron density is pulled toward the more electronegative O atom. Here, the bond polarities are *not* counterbalanced, because the water molecule is V shaped (also see Figure 4.1). Instead, the bond polarities are partially reinforced, and the O end of the molecule is more negative than the other end (the region between the H atoms), which the electron density model shows clearly:



(The molecular polarity of water has some amazing effects, from determining the composition of the oceans to supporting life itself, as you'll see in Chapter 12.)

In the two previous examples, molecular shape influences polarity. When different molecules have the same shape, the nature of the atoms surrounding the central atom can have a major effect on polarity. Consider carbon tetrachloride ( $\text{CCl}_4$ ) and chloroform ( $\text{CHCl}_3$ ), two tetrahedral molecules with very different polarities. In  $\text{CCl}_4$ , the surrounding atoms are all Cl atoms. Although each C—Cl bond is polar ( $\Delta\text{EN} = 0.5$ ), the molecule is nonpolar ( $\mu = 0 \text{ D}$ ) because the individual bond polarities counterbalance each other. In  $\text{CHCl}_3$ , H substitutes for one Cl atom, disrupting the balance and giving chloroform a significant dipole moment ( $\mu = 1.01 \text{ D}$ ):



### SAMPLE PROBLEM 10.9 Predicting the Polarity of Molecules

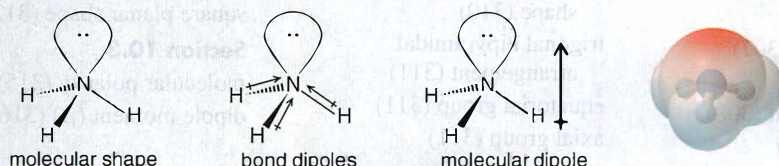
**Problem** From electronegativity (EN) values and their periodic trends (see Figure 9.20), predict whether each of the following molecules is polar and show the direction of bond dipoles and the overall molecular dipole when applicable:

- (a) Ammonia,  $\text{NH}_3$       (b) Boron trifluoride,  $\text{BF}_3$   
 (c) Carbonyl sulfide, COS (atom sequence SCO)



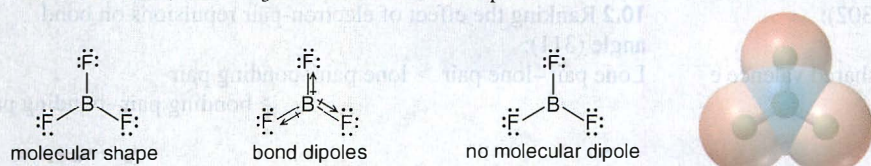
**Plan** First, we draw and name the molecular shape. Then, using relative EN values, we decide on the direction of each bond dipole. Finally, we see if the bond dipoles balance or reinforce each other in the molecule as a whole.

**Solution (a)** For  $\text{NH}_3$ . The molecular shape is trigonal pyramidal. From Figure 9.20, we see that N (EN = 3.0) is more electronegative than H (EN = 2.1), so the bond dipoles point toward N. The bond dipoles partially reinforce each other, and thus the molecular dipole points toward N:



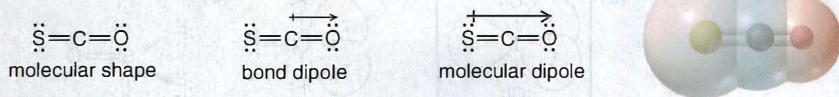
Therefore, ammonia is polar.

**(b)** For  $\text{BF}_3$ . The molecular shape is trigonal planar. Because F (EN = 4.0) is farther to the right in Period 2 than B (EN = 2.0), it is more electronegative; thus, each bond dipole points toward F. However, the bond angle is  $120^\circ$ , so the three bond dipoles counterbalance each other, and  $\text{BF}_3$  has no molecular dipole:



Therefore, boron trifluoride is nonpolar.

**(c)** For  $\text{COS}$ . The molecular shape is linear. With C and S having the same EN, the  $\text{C}=\text{S}$  bond is nonpolar, but the  $\text{C}=\text{O}$  bond is quite polar ( $\Delta\text{EN} = 1.0$ ), so there is a net molecular dipole toward the O:



Therefore, carbonyl sulfide is polar.

**FOLLOW-UP PROBLEM 10.9** Show the bond dipoles and molecular dipole, if any, for (a) dichloromethane ( $\text{CH}_2\text{Cl}_2$ ); (b) iodine oxide pentafluoride ( $\text{IOF}_5$ ); (c) nitrogen tribromide ( $\text{NBr}_3$ ).

## SECTION SUMMARY

Bond polarity and molecular shape determine molecular polarity, which is measured as a dipole moment. When bond polarities counterbalance each other, the molecule is nonpolar; when they reinforce each other, even partially, the molecule is polar.

## For Review and Reference (Numbers in parentheses refer to pages, unless noted otherwise.)

### Learning Objectives

To help you review these learning objectives, the numbers of related sections (§), sample problems (SP), and end-of-chapter problems (EP) are listed in parentheses.

1. Use the octet rule to draw a Lewis structure from a molecular formula (§ 10.1) (SPs 10.1–10.3) (EPs 10.1, 10.5–10.8)
2. Understand how electron delocalization explains bond properties, and draw resonance structures (§ 10.1) (SP 10.4) (EPs 10.2, 10.9–10.12)
3. Describe the three exceptions to the octet rule, draw Lewis structures for them, and use formal charges to select the most

important resonance structure (§ 10.1) (SP 10.5) (EPs 10.3, 10.4, 10.13–10.24)

4. Describe the five electron-group arrangements and associated molecular shapes, predict molecular shapes from Lewis structures, and explain deviations from ideal bond angles (§ 10.2) (SPs 10.6–10.8) (EPs 10.25–10.49)

5. Understand how a molecule's polarity arises, and use molecular shape and EN values to predict the direction of a dipole (§ 10.3) (SP 10.9) (EPs 10.50–10.55)